Constitution of Portland Cement Clinker

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MODERN developments in the technique of the identification and measurement of phases are shown to underlie recent advances in our understanding of the constitution of Portland cement clinker. Researches on glass in clinker have revealed its nature as a metastable phase and provided means for its approximation. Investigations have shown that commercial clinkers vary in glass content over a wide range and that the amount of this phase is profoundly affected by the rate at which the clinker is cooled through the higher temperatures. Equations have been developed by which the constitution of a clinker of known glass content may be calculated under given assumptions of the course of crystallisation. The fate of the alkalis is still undetermined, but their importance in affecting the clinker constitution is becoming recognised. A number of the effects on cement properties resulting from the presence of glass are discussed.

Elements of Progress

On January 14, 1918, the Faraday Society sponsored a symposium, international in character, on " The Setting of Cements and Plasters " (*Trans. Faraday Society*, 1919, 14, 1–69). Among the contributors were Le Chatelier of France, Desch and Donnan of England, and Rankin and Klein of the United States. Although most of the discussion bore upon the processes of setting and hardening, the constitution was not neglected and the record may be taken as a true picture of the state of the science at that date. There cannot be said to have been any precise knowledge of the constitution of clinker prior to the microscopic examinations of Le Chatelier[1] and of Törnebohm.[2] These examinations were substantially in agreement with respect to the classification of phases, denoted by Törnebohm alite, belite, celite, felite and an isotropic residue, but the chemical nature of the phases has remained a matter of controversy up to recent years. Scores of papers have been written on " What is Alite " ? Within the last decade it has been described as a lime-enriched dicalcium silicate,[3] a solid solution of lime-rich aluminate and silicate,[4] a solid solution of $3CaO . SiO_2$ and $3CaO . Al_2O_3$,[5] a solid solution of $8CaO . Al_2O_3 . 2SiO_2$ and $2CaO . SiO_2$,[6] and essentially $2CaO . SiO_2$.[44]

Alite was considered to be $3CaO . SiO_2$ by Le Chatelier[7] in 1884 and this view has been confirmed by the investigations of Rankin and Wright[8] who demonstrated the existence of the compound, Bates and Klein[9] who showed its existence in clinker, Hansen and Brownmiller[10] who identified its presence in clinker by X-ray means, Guttmann and Gille[11] who separated the alite from clinker, and many others. But in 1931, conceding the evidence of the X-ray, Guttmann[12] closed the book with the exclamation " At last the fifty-year-old question ' What is Alite ? ' is answered." A year later Jänecke[13] withdrew his entry, $8CaO . Al_2O_3 . 2SiO_2$, and half a century after the original announcement of Le Chatelier the alite of clinker is generally acknowledged to consist " essentially " of tricalcium silicate.

Modern progress is the result chiefly of advances in the technique of systematic study. Little could have been accomplished without the generalisations provided by an application of the phase rule within the various systems encountered in the complex of cement clinker. But the successful application requires tools for

[1] LE CHATELIER, H. Compt. rend., 1882, 94, 13. *J. Soc. Chem. Ind.*, 1882, I, 151. " Experimental Researches on the Constitution of Portland Cement," translated into English by Mack, J. L., New York, 1905.
[2] TÖRNEBOHM, A. E. *Tonind. Ztg.*, 1897, 21, 1148. *Baumaterialienkunde*, 1910–1911. 6, 142. *Zement*, 1903, 4, 287.
[3] DYCKERHOFF, W. *Zement*, 1927, 16, 735.
[4] KÜHL, H. *Tonind. Ztg.*, 1929, 53, 1575.
[5] GUTTMANN, A., & GILLE, F. *Zement*, 1927, 16, 921 ; 1928, 17, 296.
[6] JÄNECKE, E. *Prot. Ver. deut. Portl. Zem. Fabr.*, 1928, 51, 8.
[7] MACK, J. L., Compt. rend., 1884, 94, 13.
[8] RANKIN, G. A., & WRIGHT, F. E. *Am. J. Sci.*, 1915 (4), 39, 1.
[9] BATES, P. H., and KLEIN, A. A. *Bur. St. Tech. Papers*, No. 78, 1917.
[10] HANSEN, C. W., & BROWNMILLER, L. T. *J. Am. Ceramic Soc.*, 1928, 11, 68.
[11] GUTTMANN & GILLE. *Zement*, 1929, 18, 911.
[12] GUTTMAN & GILLE. *Zement*, 1931, 20, No. 7.
[13] JÄNECKE, E., & BRILL, R. *Zement*, 1932, 21, 380.

the positive identification of the phases that are produced by the heat treatments. The microscope was used by Le Chatelier and Törnebohm, but improvements and new developments in its use have opened up vastly greater possibilities in the resolution and identification of the clinker constituents. The X-ray was first applied to cement research in 1927,[14] but already it has become indispensable in the recognition of the cement compounds and in the still more basic understanding of the atomic rearrangements that occur in the cement kiln. To these should be added the fundamental information on phases gained by the study of heating curves[15] and heats of solution,[16] the analytical insight made possible by the test for free lime,[17] and other tools that are still in the process of development.

Twenty years ago clinker was conceded to be a mixture of compounds or solid solutions. The nature of the constituent phases was in dispute, but some progressive investigators[18] were convinced that they included $3CaO . SiO_2$, $2CaO . SiO_2$ and $3CaO . Al_2O_3$. Nothing was known of the disposition of the iron, the magnesia or the alkalis. Glass was not recognised, and the completeness of the reactions in the kiln was gauged chiefly by the soundness test in one form or another. Control in manufacture was obtained through the use of empirical oxide ratios combined with the soundness test and other tests on the cement. The first paper had just been published[9] setting forth some of the hydraulic properties of these cement compounds, but little was known of the control of cement quality through a control of the constituent compounds.

The Identification of Phases

The prime requirement in a study involving the differentiation of phases, which may include glass, solid solutions, and minor compounds, is a means for their proper identification and measurement. The petrographic miscroscope in in the past has not been altogether adequate for this task, but new developments give promise that satisfactory methods will become available. In recent years the X-ray has become one of the most reliable tools for the identification of compounds and has been of prime value in advancing the knowledge of cement chemistry. The discovery of a metastable glassy phase, having an X-ray pattern similar to that of a crystalline compound, though unrelated chemically, has opened a field for research of a fundamental character. Such studies may not be justified by any prognosticated application to the improvement of cement manufacture, but it is the experience of industry that results obtained by such studies find use continuously and make for advances in scientific technology.

It was first demonstrated by Tavasci[19] that polished sections of clinker, properly etched and viewed with reflected light, are well suited for a study of the cement compounds. This subject has been materially advanced by Insley[20]

[14] HARRINGTON, E. A.   *Am. J. Sci.*, 1927 (5), 13, 467.
[15] HANSEN, C. W.   *Bur. Sts. J. Res.*, 1930, 4, 55 ; RP 132.
[16] LERCH, WM., & BROWNMILLER, L. T.   *Bur. St. J. Res.*, 1937, 18, 609 ; RP 997.
[17] LERCH, WM., & BOGUE, R. H.   *Ind. Eng. Chem.* (Anal. Ed.), 1930, 2, 296.
[18] *Trans. Far. Soc.*, 1919, 14, 1–69.
[19] TAVASCI, B.   *Giron. chim. ind. applicata*, 1934, 16, 538.
[20] INSLEY, H.   *Bur. St. J. Res.*, 1936, 17, 353 ; RP 917.

PLATE I.—Photomicrograph of polished section of clinker No. 3Q showing $3CaO.SiO_2$ (large clear crystals), $2CaO.SiO_2$ (rounded striated grains), $4CaO.Al_2O_3.Fe_2O_3$ (white interstitial material), and glass (dark interstitial material), the form of which is determined by the crystallization of $4CaO.Al_2O_3.Fe_2O_3$). Etched with distilled water for 5 seconds followed by 1% HNO_3 in alcohol for 2 seconds. Magnification 1000x. (Ward.)

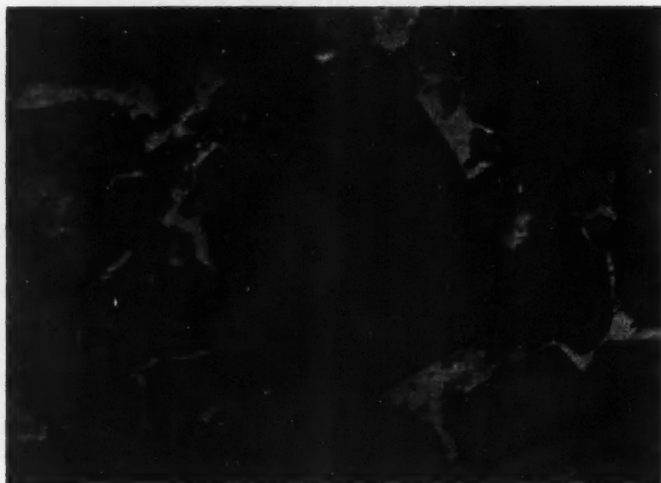

PLATE II.—Photomicrograph of polished section of clinker No. 6S selected to show $3CaO.Al_2O_3$, the large crystal at centre. Etched with distilled water for 5 seconds followed by 1% HNO_3 in alcohol for 2 seconds. Magnification 1000x. (Ward.)

and Ward[21]. The specimen is generally impregnated with a resin (Bakelite No. Br. 0014 has been found suitable) and, after grinding, polished with a paste of rouge with water or alcohol on a rotating lap of coarse duck cloth. The best general etching solution for clinker has been found to be a 1-per cent. solution of nitric acid in ethyl alcohol, the specimen being immersed about 5 seconds.[20] For special purposes, however, different etchants are required.

The photomicrograph of *Plate* I shows a polished section of clinker in which the major phases are easily distinguishable. The large crystals with hexagonal outlines are $3CaO . SiO_2$. These often show zonal structure which suggests some degree of solid miscibility and sometimes also simple twinning. In thin sections of commercial clinker, interference figures of tricalcium silicate frequently depart considerably from perfect uniaxiality,[20] while sections of crystals oblique to the optic axis often exhibit a change in extinction angle from interior to exterior of the crystal.[22] Variations have been observed in the index of refraction of tricalcium silicate obtained from basic open-hearth slags. These have been attributed to solid solution.[23] The X-ray diffraction pattern of the $3CaO . SiO_2$ in clinker has also been observed to be slightly shifted from the position in the pure compound.[20] Substantiating evidence of solid solution has not been obtained, however, in equilibrium studies on systems of pure components.

The rounded heavily-striated grains are dicalcium silicate. Sundius[24] believed these to be the α-form, characterised by two sets of fine polysynthetic twinning bands meeting at a steep angle. The β-form (obtained in synthetic preparation heated below the α—β inversion temperature, 1,420 deg.), was characterised in his opinion by a single set of polysynthetic bands. Insley has pointed out, however, that the complex twinning found in clinkers that have been heated above 1,420 deg. may be, in reality, only an indication that the crystal has at some time been in the α-state and offers as confirmation that the X-ray patterns of specimens heated above 1,450 deg. and of similar specimens heated at 1,375 deg. are identical. He differentiates three types of β-$2CaO . SiO_2$: Type I, containing 2 or 3 sets of interpenetrating striations, each set being composed of parallel bands, obtained from compositions which have been heated above 1,420 deg.; Type II, containing 1 set of polysynthetic bands, obtained from compositions which have been heated only to temperatures below the α—β inversions; and Type III, containing no twinning bands, obtained only when moderately slow cooling below the α—β inversion temperature has been permitted before quenching.

The light material which occurs between the grains of the silicates has been identified as $4CaO . Al_2O_3 . Fe_2O_3$ or a solid solution of $4CaO . Al_2O_3 . Fe_2O_3$ with $2CaO . Fe_2O_3$ if the composition is such that an excess of Fe_2O_3 is present.[20] A small amount of MgO also enters into solid solution with the $4CaO . Al_2O_3 . Fe_2O_3$.

[21] WARD, G. W.   Unpublished data.
[22] BROWN, L. S.   Personal communication.
[23] ANDERSON, O., & LEE, H. C.   *J. Wash. Acad. Sci.*, 1933, 23, 338.
[24] SUNDIUS, N.   *Z. anorg. allgem. Chem.*, 1933, 213, 343.

Schwiete and zur Strassen[25] limit this to 2 per cent., but Insley and McMurdie[26] believe the solubility is not greater than 1 per cent.   McMurdie[27] also finds that $4CaO . Al_2O_3 . Fe_2O_3$ may take up between 3 and 5 per cent. of the calcium aluminates in solid solution.   This phase occurs almost universally as prisms which are larger as the $Al_2O_3 : Fe_2O_3$ ratio is diminished and the cooling prolonged. It is scarcely affected by the etchant (1 per cent. HNO_3 in alcohol), and has high reflectivity.

The dark irregular interstitial material, closely associated with $4CaO . Al_2O_3 . Fe_2O_3$, is considered to be glass.[26]   It is more readily etched by distilled water than the silicates and has a much lower reflectivity than the $4CaO . Al_2O_3 . Fe_2O_3$. Ward [21] has found that it is etched readily by a 1-per cent. solution of nitric acid in alcohol.   It is usually isotropic, but its composition and optical properties are probably dependent on the composition of the clinker and the heat-treatment to which it has been subjected.

Tricalcium aluminate has been observed in polished sections of a few commercial clinkers, [21, 26] as large rectangular crystals, nearly or altogether isotropic, enclosing crystals of silicates.   A photomicrograph of this material is shown in *Plate* II. It is etched readily by water in 2 or 3 seconds and less readily by a 1-per cent. solution of nitric acid in alcohol.   Through the development of a greatly improved technique in the making of thin sections, Brown[28] had previously observed a phase, somewhat similar but generally of greater size, in laboratory clinkers having an $Al_2O_3 : Fe_2O_3$ ratio above 1·38.   Usually, however, the large crystals could not be seen in commercial clinkers, but their presence was indicated by a mass birefringence of the $4CaO . Al_2O_3 . Fe_2O_3$.

There is also observed in the dark interstitial material of some clinkers a prismatic phase[26, 21] which may be readily distinguished from the amorphous glassy phase by its crystalline form and by its more rapid etching with distilled water.   Examination of polished thin sections shows that these crystals have a low but distinct birefraction of about the order of $3CaO . SiO_2$.   A photomicrograph of this phase is shown in *Plate* III.

In the course of a preliminary study to learn the nature of this material[26] a laboratory preparation was made consisting of CaO, Al_2O_3, SiO_2 and Fe_2O_3 in about the proportions in which they occur in Portland cement clinker.   This was heated to 1,450 deg. and cooled slowly.   The clinker showed no prismatic dark interstitial material   The same mix was again clinkered with additions of alkali carbonates to give in the resulting mixtures 1·5 per cent. Na_2O and 1·5 per cent. K_2O respectively.   The clinkers obtained showed prismatic crystals which appeared to be identical with those previously observed in the commercial clinkers.   The optical properties of the prismatic phase agree with those of the compound $8CaO . Na_2O . 3Al_2O_3$[29] with the exception of having higher indices of refraction which may be due to some Fe_2O_3 in solid solution.[26]

[25] SCHWIETE, H. E., & ZUR STRASSEN, H.   *Zement*, 1934, 23, 511.
[26] INSLEY, H., & McMURDIE, H. F.   *Bur. St. J. Res.*, 1938, 20, 173 ;   RP 1074.
[27] McMURDIE, H. F.   *Bur. St. J. Res.*, 1937, 18, 475 ;   RP 987.
[28] BROWN, L. S.   *Proc. Am. Soc. Testing Materials*, 1937, 37, 277.
[29] BROWNMILLER, L. T., & BOGUE, R. H.   *Am. J. Sci.*, 1932, 23, 501.
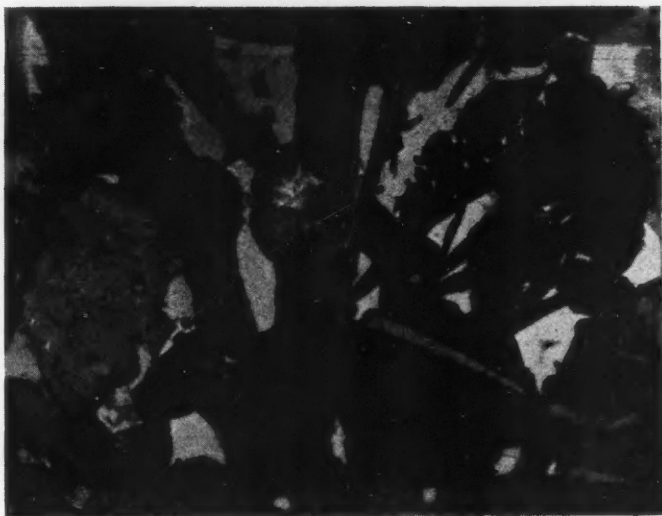
PLATE III.—Photomicrograph of polished section of clinker No. 2S selected to show the prismatic dark interstitial phase. Etched with distilled water for 5 seconds followed by 1% HNO$_3$ in alcohol for 2 seconds. Magnification 1000x. (Ward.)

PLATE IV.—Photomicrograph of polished section of clinker No. 4Q selected to show grains of free CaO. Etched with 1 : 3 water-alcohol for 60 seconds. Magnification 1000x. (Ward.)

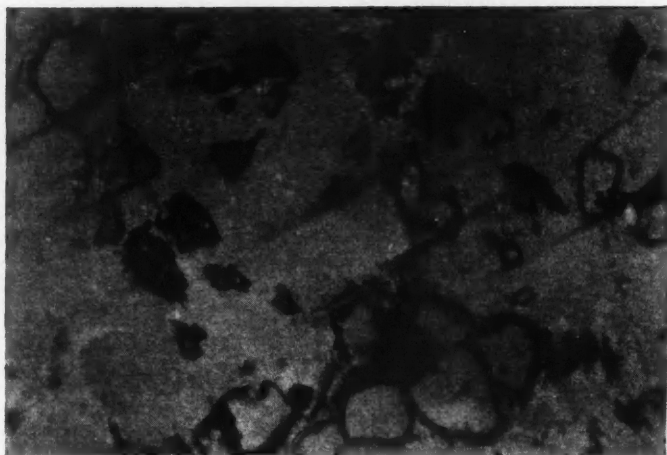PLATE V.—Photomicrograph of polished section of clinker No. 3S selected to show grains of periclase as observed in slowly-cooled clinkers. No etch. Magnification 1000x. (Ward.)
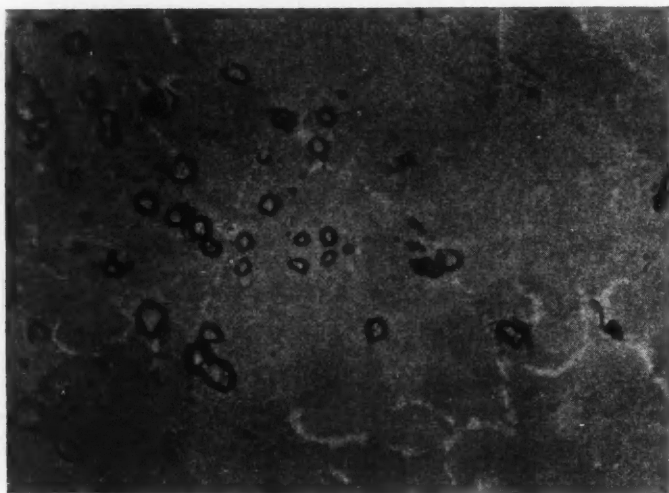

PLATE VI.—Photomicrograph of polished section of clinker No. 3Q selected to show grains of periclase as observed in quickly-cooled clinkers. No etch. Magnification 1000x. (Ward.)

Insley found that the ternary compound of CaO, Na_2O and Al_2O_3 forms a complete solid solution series with $3CaO . Al_2O_3$ provided ample time is allowed for the action to take place.[30] Taylor[31] has observed that, when quenches of compositions on the join $3CaO . Al_2O_3$-$8CaO . Na_2O . 3Al_2O_3$ or within the triangle $3CaO . Al_2O_3$-$8CaO . Na_2O . 3Al_2O_3$-$5CaO . 3Al_2O_3$ are made along the liquidus, or when cooling from 1,500 deg. to 1,425 deg. has been rapid, there are found both $3CaO . Al_2O_3$ and the alkali compound as independent phases. In charges which are cooled slowly and contain little or no glass, $3CaO . Al_2O_3$ crystals are not observed, but instead a single solid solution phase in which the birefraction decreases as the calculated amount of $3CaO . Al_2O_3$ increases.

These observations suggest that the soda component of the prismatic dark interstitial material of clinker may contain or consist of a ternary compound of CaO, Na_2O and Al_2O_3 or a solid solution of that compound with $3CaO . Al_2O_3$. It is probable also that a small amount of $4CaO . Al_2O_3 . Fe_2O_3$ enters into the phase as evidenced by an increase in the refractive index of the alkali compound in the presence of $4CaO . Al_2O_3 . Fe_2O_3$.[26] The common juxtaposition, however, of the prismatic phase with the light interstitial material indicates that the amount of solution of the $4CaO . Al_2O_3 . Fe_2O_3$ in the alkali compound is limited if, indeed, the prismatic phase is of this general composition, but further exploration of the field is required to establish the complete phase relationships involved.

The potash compound stable in the CaO-K_2O-Al_2O_3 system is $K_2O . Al_2O_3$.[32] It is not yet clear what part this compound may play in the formation of the prismatic phase or if a different compound or solid solution is formed with some of the other constituents of Portland cement clinker.

The problem of the alkalis is discussed further later.

Free CaO may occur in clinker either in aggregates or in single grains which often occur at the centre of the $3CaO . SiO_2$ crystals.[26] The grains are etched easily by water and appear as slightly darkened round areas. A photomicrograph is shown in *Plate* IV.

Periclase (free MgO) appears as irregular-shaped grains which are not readily etched with water and may be observed on unetched polished sections because of their high reflectivity.[26] Special care in polishing is necessary, however, because the grains are easily fragmented and the cracks filled with polishing medium. It is found mainly in the interstitial material, but may occur as inclusions in the silicates. In *Plate* V is shown a photomicrograph of periclase in a commercial clinker that was reheated and cooled slowly. The same clinker reheated and cooled quickly is shown in *Plate* VI. Magnesia is known to dissolve in the liquid[33] to the extent of 4 to 6 per cent. depending on the $Al_2O_3 : Fe_2O_3$ ratio. The smaller size of the grains in the quickly cooled (high glass) clinker is significant.

[30] INSLEY, H., and McMURDIE, H. F. Unpublished data.
[31] TAYLOR, W. H. Unpublished data, a part of which has been prepared for publication.
[32] BROWNMILLER, L. T. *Am. J. Sci.*, 1935 (5), 29, 260.
[33] LERCH, WM., & TAYLOR, W. H. *Concrete* (Cement Mill Ed.), 1937, 45, 199, 217.

The Wagner Turbidimeter for Measuring the Fineness of Cement.

(Concluded from September number.)

Some Causes of Error

An attempt was made to discover some of the causes of error and, at the same time, efforts were made towards the elimination of these causes. The two causes of error may be divided into two groups : (*a*) errors which relate to the experimental method, and (*b*) errors which appear when the method is applied to different cements.

(*a*) ERRORS INHERENT IN EXPERIMENTAL METHOD.—The following causes of error inherent in the experimental method were studied by experiment : The sieve No. 325 ; The influence of the intensity of the light ; Defects of the cell and of the micro-ammeter ; Errors in the first reading ; Graduation of the test tube and smallness of the sample to be tested.

Sieve No. 325.—It was observed that in the application of the formula which gives the specific area there enters as a numerator the percentage *r* of the material which passed through sieve No. 325. The error in *S* originating from an error in *r* is therefore equal to the latter in a relative value. The error which might be made in obtaining *r* does not exceed, as a rule, 3 per cent. of the screened material or 3·5 per cent. of the material passing through the screen. The influence of the error in the screen is therefore comparatively small (as a rule, less than 4 per cent. in relative value).

Intensity of light.—The greater the intensity of light the smaller will be the value of the specific area resulting from the calculations made following the formula already given, so that it is necessary, in accordance with the hypothesis which served as a basis for the establishment of that formula, to regulate the intensity of light in such a way that the intensity I_0 of the current generated by the cell (when the beam of light only just passes through the container with clean kerosene) will be exactly equal to 100 micro-amperes.

In order to study the influence of an error in the regulation of the luminous intensity on the specific area, making use of the results obtained in tests, *Fig.* 2 was prepared in which I_1 represents the intensity of light through the filter, and from this the conclusion was reached that a variation of 1 micro-ampere in I_1 corresponds to a variation of 32 square cm. per gramme (approximately) in the specific area, using the same cement. As in this case I_0 is practically equal to $4 \times I_1$, an error of 1 micro-ampere in I_0 would almost correspond to an error of nearly 8 square cm. per gramme in the specific area. The way to reduce an error due to an incorrect value of the luminous intensity lies in the careful regulation of the apparatus, and this can be carried out in a few seconds using the method recommended.

Defects of the cell and of the micro-ammeter.—The current generated by the cell should bear an exact relation to the intensity of the light produced, as this has

been admitted by the theory of the method or system. It does not matter if the current is read in micro-amperes or in any other unit of a different value, provided the selected unit is correct and exact, as the relation of the readings (turbidity) must always be maintained ; it is indispensable, however, that the readings should be in proportion to the luminous intensities. This is a delicate point of the apparatus, as the first photo-electric cells specially made for the turbidimeter did not fulfil this condition satisfactorily. The selenium cells (Western Photronic) fitted to the turbidimeter experience, after a certain period, a sudden modification in their internal resistance, thus reducing considerably their efficiency, and the relation between the luminous intensity and the current is no longer in line[1].
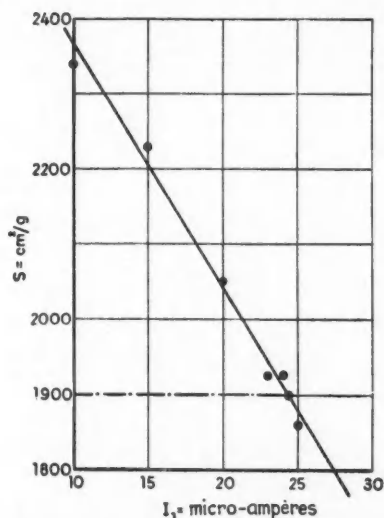
Fig. 2.—Influence of the intensity of the light.

Another point which deserves special attention is the micro-ammeter, as this instrument, owing to its delicate nature, might get out of adjustment, giving wrong indications. This defect might give rise to serious difficulties, as it might be overlooked by the operator, and the lack of adjustment could only be noticed subsequently through the comparison of the results obtained using other instruments. To emphasise the importance to be given to the use of a well regulated micro-ammeter, it will be sufficient to mention that an error of 0·1 micro-ampere in the value of I_{60} equals an error of nearly 2 per cent. in the specific area, as is explained later.

First reading.—Another possible cause of error is in the first reading (I_{60}). In the application of the formula the first reading (I_{60}) greatly influences the

[1] At the present time the Western Company is manufacturing a special cell for this instrument (model 594, No. 69765-18). This cell is carefully controlled with regard to its proportional characteristics.

final result, and it has therefore to be done with care and precisely at the moment fixed for the passage of kerosene in the corresponding mark of the test tube.

In the formula we have as numerator the expression $(2 - \log. I_{60})$ and, as denominator, the expression $(11 \cdot 5 \log. I_{60})$. From the large number of results registered the conclusion is reached that the denominator of the formula represents, on average, $1 \cdot 3$, varying between $1 \cdot 0$ and $1 \cdot 6$. Generally speaking, the first reading is of the order of 15 micro-amperes, equal to $\log. I_{60} = 1 \cdot 176$.

The precision with which the readings of the micro-ammeter can be made is of the order of $0 \cdot 1$ micro-ampere. For such a difference in the first reading the resulting error will be

(1) in the numerator :

$$\frac{1 \cdot 176 - 1 \cdot 179}{2 - 1 \cdot 176} \times 100 = \frac{0 \cdot 29}{0 \cdot 824} = 0 \cdot 35 \text{ per cent.}$$

(2) in the denominator :

$$\frac{11 \cdot 5 \times 0 \cdot 29 \times 100}{1 \cdot 3} = 2 \cdot 5 \text{ per cent.}$$

As these errors are in opposite directions, it can be stated that the resulting error in the specific area amounts to 2 per cent. in the case of an error of barely $0 \cdot 1$ micro-ampere in the first reading. If this reading is not carefully taken, the error will easily be 5 per cent.

Graduation of the test tube.—Between two series of test results obtained on different days there is a certain divergence, even of a small nature. This can probably be attributed to small variations in the characteristics of the kerosene used or to differences in the temperature of the atmosphere ; both causes give rise to modifications in the density and viscosity of the kerosene[1]. This fact is equal to an erroneous reading in the test tube, as the test tube has been graduated for kerosene of given density or viscosity. On the other hand, the draining speed of the kerosene is also subject to variation and some compensation, at least of a partial nature, takes place. This is a rather small point, but it is mentioned to give an idea of the many causes of error, thus justifying certain discrepancies in the results which sometimes occur without apparent cause. In such cases it may be that numerous small errors also take place, accumulating through the indirect process followed in accordance with the method adopted.

Quantity of the sample.—Another disadvantage of the method used is the smallness of the sample. The test is carried out with barely $0 \cdot 3$ gramme of cement. No matter how carefully homogenised a sample may be, it can never be stated that the $0 \cdot 3$ gramme withdrawn for test purposes is, in fact, an average sample. It is chiefly when the cement is partly hydrated that the results obtained with the turbidimeter lose all their significance through the smallness of the sample. To take an example : A partly hydrated cement, of which the residue on the sieve amounted to $21 \cdot 4$ per cent., gave through the turbidimeter a specific area of $S = 1,780$ square cm. per gramme. Judging from the specific area the

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[1] P. J. Freeman (*Pit and Quarry*, August, 1938).

cement appeared to possess a satisfactory fineness, but nevertheless was a long way away from the specification (residue 15 per cent.).   When the cement is partly hydrated, because it is not possible to obtain a good dispersion in suspension the tests fail to give concordant results, although their average as a rule corresponds to a value in excess of the true value by virtue of the fact that it is necessary to eliminate the lumps of hydrated cement.

Deflaking element.—In the preparation of the suspension solution 5 drops of oleic acid are introduced to act as a deflaking element to facilitate the dispersion of the particles.   Oleic acid, however, easily oxidises when exposed to air and, after it has become oxidised, acts as a flaking instead of a deflaking factor.   The use of an oxidised oleic acid entirely destroys the tests, giving exaggerated values for the specific area, which in some cases are 100 per cent. higher than the actual values.   In the following table are indicated the results obtained with two kinds of oleic acid, one of them oxidised and the other free from oxidation, thus

SAMPLE 1 F-9—I.P.T. $r = 85 \cdot 6\%$.

TESTS		Specific Area in cm²/g				Average
		1	2	3	4	
Oxidised Oleic Acid	..	3,380	3,160	3,310	3,315	3,291
Pure Oleic Acid ..	..	1,625	1,626	1,615	1,640	1,626

giving an idea of the importance of this factor.   As it is not convenient to keep large quantities of oleic acid in the laboratory, in view of the fact that it becomes so easily oxidised, and because pure acid is difficult and dear to buy, this method is a further serious difficulty.

TABLE XII.
INFLUENCE OF OLEIC ACID.

Samples	Residues (%) on Sieves		Specific Area in cm²/g (Average of Two Test Results)		Differences between Two Averages	Maximum Differences between Two Test Results	
	No. 325	No. 200	With Oleic Acid	Without Oleic Acid		With Oleic Acid	Without Oleic Acid
1	22·7	12·4	1,310	1,310	0	26	18
2	24·0	15·4	1,360	1,220	140	58	24
3	24·0	9·2	1,370	1,290	80	68	67
4	21·3	20·8	1,510	1,520	— 10	33	26
5	25·2	11·4	1,570	1,290	280	6	96
6	16·5	10·0	1,640	1,560	80	10	3
7	14·4	7·2	1,680	1,570	110	18	37
8	15·2	9·0	1,700	1,560	140	20	109
9	16·0	8·1	1,710	1,690	220	33	68
10	17·0	11·3	1,790	1,550	240	65	83
11	13·7	8·2	1,820	1,580	240	37	47
12	12·5	7·0	1,850	1,560	190	24	75
13	7·3	3·3	2,360	2,180	180	22	49
14	7·7	1·7	2,450	2,290	160	9	50

NOTE.—The values indicated are the average of five tests.

In *Table* XII are given the results of tests made with 14 samples of different brands of cement, comparing the results obtained with and without the use of oleic acid. The results have been presented in increasing order of the specific area of the samples; for the purpose of comparison, the table indicates the degrees of fineness determined by sieves Nos. 325 and 200. From these results it is possible to conclude that (a) the introduction of oleic acid increases the value found as representing the specific area; this was to be expected, as the function of the acid is to facilitate the dispersion; and (b) the introduction of the deflaking element is advantageous as it affords a greater reproductivity of the results. The dispersions obtained are homogeneous.

ERRORS ORIGINATING FROM THE VARIETY OF DIFFERENT CEMENTS.—These causes of errors are due to the variation of some physical characteristics of the cements, to the specific mass, the colour, the reflecting power, the transparency, the geometrical shape of the particles and their dimensions, etc. As a consequence of the variety of these qualities, the results obtained for two different cements differ from the exact values in ways which are also different—and it remains to determine the importance of the influence of the variation of these qualities on the results.

Specific mass.—The calculation of the specific area is made using the formula

$$S = \frac{38 \, r \, (2 - \log I_{60})}{1 \cdot 5 + 0 \cdot 75 \log I_{7 \cdot 5} + \log I_{10} + \ldots \ldots + \log I_{55} - 11 \cdot 5 \log I_{60}}$$

which has a constant factor 38. In the deduction of the formula, this factor 38 varies in inverted relation to the specific mass of the particles. Portland cements have a variable specific mass of from 3 to 3·2 grammes per square centimetre. In this formula the factor 38 corresponds to the specific mass of 3·16, and should therefore vary within the limits

$$38 \times \frac{3 \cdot 16}{3 \cdot 00} = 40 \cdot 0 \text{ and } 38 \times \frac{3 \cdot 16}{3 \cdot 20} = 37 \cdot 5$$

To examine the influence of this difference in a practical case, determining the specific area of a Portland cement and using the factor 38 we obtained $S = 1{,}850$ square cm. per gramme; if the specific mass of this cement were 3·00 and not 3·16, its area should be

$$S = 1{,}850 \times \frac{3 \cdot 16}{3 \cdot 00} = 1{,}949 \text{ square cm. per gramme.}$$

If the specific mass were 3·20, the specific area would be

$$S = 1{,}850 \times \frac{3 \cdot 16}{3 \cdot 20} = 1{,}827 \text{ square cm. per gramme.}$$

It may happen, therefore, that two different cements, which actually differ with regard to the specific area from $1{,}949 - 1{,}827 = 112$ square cm. per gramme, when tested by the turbidimeter will show the same value for this characteristic, because as a rule the exact values of the respective specific masses are not taken into account. The relative error resulting in the specific area might amount, as a maximum, to

$$\frac{40 - 38}{40} \times 100 = 5 \text{ per cent.}$$

The way to eliminate this error is simple, as it is sufficient to determine and to take into account the specific mass of each sample. The specific mass of cement of the same origin remains fairly constant, but for the purpose of comparing various types of cement it is necessary to take into account the actual value of its specific mass in order to obtain more significant values of the respective specific areas.

Colour of different cements.—As mentioned previously, there is no method of determining exactly the absolute value of the area of such small and irregularly shaped particles as the particles of Portland cement. In the case of particles above a certain size the method which appears to give the nearest appreciation of the actual values is the microscope method[1]. In studying the results obtained with this method, it is seen that in the case of dark cements the results obtained through the turbidimeter agree fairly satisfactorily with the results obtained through the microscope. In the case of ash-coloured cements the values obtained through the turbidimeter are low, whilst the results with white cements show high values. Judging from the results obtained by Wagner (A.S.T.M., 1933, Volume 33, Part II), the difference, in the case of a white cement of 2,400 square cm. per gramme, might reach + 500 square cm. per gramme (21 per cent.) ; in the case of an ash-coloured cement the difference might reach − 300 square cm. per gramme (13 per cent.). This means to say that, due to the colour, the turbidimeter might give values which will differ from the exact value in a different manner, and that results corresponding to cements of the same specific area might differ between themselves up to 800 square cm. per gramme (nearly 34 per cent. of the correct value). This alone is sufficient to affect the comparative value of the test. Wagner minimises the importance of this imperfection and questions the results obtained with the microscope, basing his arguments on the fact that the handling of the microscope is an extremely delicate matter. The correction of this defect is not easy, and there seems to be no existing means to remedy it. It may be necessary to measure directly (through the microscope, for instance) the specific area of at least a fraction of the cement separated, and to deduct from this a correcting factor.

Shape and dimensions of the particles.—The Wagner method has been based on Stokes's sedimentation law, which considers that all the particles of the sample in suspension are spherical. This fact creates a difference between the calculated and actual specific area, as the particles of Portland cement are irregular. It is not unreasonable to admit that this cause of error might act in an analogous manner, at least in the case of all ordinary Portland cements, failing to affect in a sensible manner the comparative value of the results obtained with the turbidimeter.

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[1] The separating power of microscopes operating with visible light does not permit us to discover with precision, and less still to measure, the particles of a diameter under 0·2 micron. The recently discovered electronic microscope has considerably increased this limit, and perhaps it will permit to attain the millimicron.

The same cannot, however, be said with regard to the granular nature of cement. From the cases presented by Wagner (see *Fig.* 3) it is seen that, in the case of white cements, the specific area of sample A (1,230 square cm. per gramme) obtained with the turbidimeter shows a difference of 40 square cm. per gramme (3 per cent.) in excess of the results obtained with the microscope, at the same time that in the case of sample E (2,400 square cm. per gramme), of a different granular nature, the difference amounts to 500 square cm. per gramme (21 per cent.) also in excess[1]. These results tend to show a systematic effect of
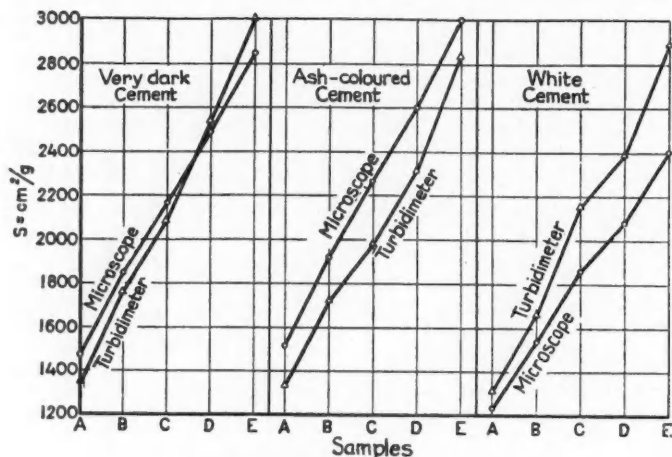

**Fig. 3.—Influence of the colour of cements,
according to Wagner.**

the dimensions of the granular formations over the indications obtained with the turbidimeter.

With regard to the samples of dark and ash-coloured cements studied by Wagner, it appears that the granular characteristics have not shown any appreciable systematic influence.

It is opportune to mention here the work of R. N. Traxler and L. A. H. Baum (*A.S.T.M.*, Vol. 35, Part II, p. 457), in which a study is made of the various factors

[1] The granular characteristics of samples A and E are as follows :

θ in microns	Percentages in Weight	
	Sample A	Sample E
0–17	15	35
7–22	15	30
22–45	15	25
45–75	25	10
> 75	30	0

which influence the determination of the granular characteristics of materials pulverised by the Wagner turbidimeter. The authors have arrived at the conclusion that no direct relation exists between the turbidity and the concentration, that is to say, between the area and the turbidity. This means that the so-called "transmittance constant" of Wagner is influenced by the dimensions of the particles and by the optical qualities of the material in suspension. The larger the particles the smaller is the transmittance[1].

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[1] The "c" values for silica and slate particles of various sizes obtained by Traxler and Baum are given below :

Dimensions of the Particles in microns	Transmittance "c"	
	White Silica	Green Slate
2	2,580	1,680
2–5	—	819
5–10	1,290	722
10–20	—	550
20–40	955	476

Recent Patents Relating to Cement.

Oil-well Cement.

502,015.   Standard Oil Development Co.   July 8, 1937.

To cement slurry is added a mixture of an aqueous solution of an alkali metal hydroxide and tannin or a tannin derivative, in sufficient quantity to retard the initial set and reduce the viscosity of the slurry.   The slurry is used to seal off walls of hollow spaces such as bore holes and pit shafts.   To a cement slurry containing 35 cc. of water per 100 gr. of cement is added a solution containing (by weight) 5 per cent. of caustic soda and 5 per cent. of quebracho, in the proportions of 1 cc. solution to 100 gr. cement.   The tannin, etc., may be used in the form of extracts, solutions, and distillates of tannins or tannates, including extracts of wood such as sumac of chestnut extracts, or as divi divi, gambier or spruce extracts, or as tannic acid or quercitannic acid, or as alkali salts of tannins.

The Specification comprises also adding to the cement slurry any organic material of feebly acidic properties, with or without alkaline hydroxide, including calcium hydroxide, e.g. humic acid, lignic acid, gallic acid, phenol compounds such as pyrogallol, extracts, solutions and distillates of lignins or of humins, alkali salts of the above substances, the lignins from the alkaline extraction of rice hulls, extracts of peat, straw and cereals, or carbo-cyclic sulphonic acids such as those obtained by the fuming acid treatment of petroleum oils as described in U.S.A. Specification 1,474,933 or those prepared from the Edeleanu extract obtained in the sulphur dioxide treatment of kerosene or other petroleum oil, or the alkali salts of these sulphonic acids.

Aluminous Cement.

503,225.   C. S. Fox.   September 28, 1937.

In the manufacture of aluminous cement, a charge consisting of bauxite, laterite, or the like, limestone or chalk, and fuel is smelted in a blast or like furnace, the iron is recovered, and the slag is adjusted as to proportions of ingredients in a second furnace, some or all of the ingredients being briquetted into lumps to resist crushing and abrasion in the first, and if desired, both stages.   Bauxite, laterite, or like alumina and iron-containing material of low silica content, is intimately mixed with fluxing material in such proportions as to yield an eutectic slag of approximately 49.5 per cent. of lime, 43.7 per cent. of alumina, and 6.8 per cent. of silica, and is briquetted with aluminous cement, preferably the cement of the invention.   Additional iron ore may be added to increase the yield of metal.   The lumps may be preheated, and are then smelted in a blastfurnace. The slag is run off into adjusting furnaces, containing materials, preferably already fused, and which may have been preliminarily briquetted, which will give a melt containing approximately 48 parts of alumina, 42 parts of lime, and 7 parts of silica, and the whole is heated and agitated until homogeneous.   The melt is cast into slabs, preferably in metal trays, and finely ground.

Porous Artificial Stone.

502,780.   K. I. A. Eklund.   July 23, 1938.

An alloy of aluminium with an alkali-soluble metal is used as gas-generating agent in the manufacture of light-weight stone.   The alloy is added to a mortar comprising a calcareous and a siliceous ingredient with water and a small amount of a plasticising agent which reduces the amount of water required.   The mix is allowed to expand at room temperature, and is then steam cured.   Suitable aluminium alloys are those with tin, antimony, zinc and lead.   The calcareous material may be lime, basic slag, or a cement. The siliceous material may be sand or a clay.   An aggregate may be added. Suitable plasticisers are sugar, water-glass, borax, alkali, phosphates, soaps, glycerine, gelatine, organic bases, sulphonic acids, and alkali-soluble oxides and salts of amphoteric metals, for example, lead, tin, zinc, and antimony.

Black Aggregate.

502,376.   A. P. Laurie.   November 27, 1937.

The residue left after the removal of alumina from bauxite is mixed with a flux and heated to form a black aggregate for concrete.   The residue may be mixed with 5 to 10 per cent. of silica and 5 to 10 per cent. of felspar, heated to 1200 to 1220 deg. C., and crushed.   The colour may be improved by the addition of manganite ore, or black oxide of manganese
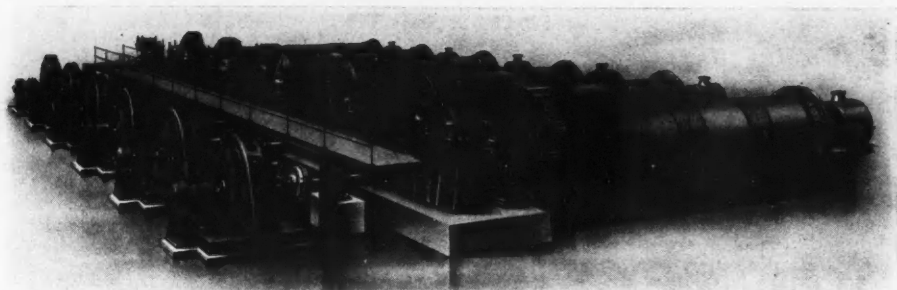
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